

LEWIS ACID IONIC LIQUIDS

RELATED APPLICATION DATA

[0001] The present application claims priority to U.S. Provisional Application No. 60/404,202, filed August 16, 2002.

FIELD OF THE INVENTIONS

[0002] The present inventions pertain to compositions comprising a Lewis acid ionic liquid and processes for making same.

BACKGROUND AND SUMMARY OF THE INVENTIONS

[0002] Ionic liquids are salts that are liquid at ambient or near ambient temperatures (i.e., having a melting point, or melting range, below about 100°C). Ionic liquids have a number of uses that include replacing organic solvents in chemical processes and reactions, extracting organic compounds from aqueous waste streams, and as electrolytes in devices such as capacitors and batteries. This is because, unlike conventional organic solvents, ionic liquids are non-volatile and non-flammable. These properties are advantageous to help reduce losses to evaporation, eliminate volatile organic emissions, and improve safety.

[0003] Other properties of ionic liquids have also proved advantageous. For example, many ionic liquids have a broad temperature range at which they remain liquid and also are stable over a broad pH range. This is beneficial for high temperature processes with a demanding pH. Further, some ionic liquid systems can be used as both a solvent and catalyst. For example, [bmim]-Al₂Cl₇ and [emim]-Al₂Cl₇ can be employed as a solvent and catalyst in Friedel-Crafts reactions wherein bmim is 1-butyl-3-methylimidazolium and emim is 1-ethyl-3-methylimidazolium.

23 [0004] For the aforementioned reasons, it would be desirable to discover new ionic liquid
24 compounds with advantageous properties. It would further be desirable if such compounds could
25 be made by simple processes with low amounts of waste and impurities.

26 [0005] Advantageously, new ionic liquid compounds have been discovered. The compounds
27 comprise a Lewis acid anion and are made via simple processes that are capable of producing
28 ionic liquids having a high purity.

29 DETAILED DESCRIPTION OF THE INVENTIONS

30 [0006] As used herein "ionic liquid" means a salt (or hydrate or solvate of the salt)
31 comprising a cation and an anion that is a liquid at ambient or near ambient temperatures (i.e.
32 having a melting point, or melting range, below about 100°C). An ionic liquid may comprise
33 two or more different salts, e.g., mixtures of salts comprising two or more different cations,
34 anions, or both. Ionic liquids can be hydrated or solvated. Thus, both hydrates and solvates are
35 considered to be within the definition of "ionic liquid."

36 [0007] As used herein "composition" includes a mixture of the materials that comprise the
37 composition, as well as, products formed by the reaction or the decomposition of the materials
38 that comprise the composition.

39 [0008] As used herein "derived from" means made or mixed from the specified materials,
40 but not necessarily composed of a simple mixture of those materials. Substances "derived from"
41 specified materials may be simple mixtures of the original materials, and may also include the
42 reaction products of those materials, or may even be wholly composed of reaction or
43 decomposition products of the original materials.

44 [0009] As used herein "halo" means chloro, bromo, fluoro, or iodo, alkyl means a
45 monovalent alkane group which may be substituted with one or more heteroatoms such as

46 nitrogen or oxygen, double bonds, or other substituents. The type of the substituent is not
47 particularly critical so long as the compound or mixture of compounds has the desired ionic
48 liquid properties. Thus, the substituents usually may include typical and non-typical organic
49 substituents such as those selected from the group consisting of alkyl, alkoxy, alkylthio, SO₃H,
50 NO₂, halo, cyano, silyl, OH, and other suitable substituents. The substituent group itself may
51 often be further substituted.

52 **[0010]** As used herein, "Lewis acid" is a substance that accepts or is capable of accepting an
53 electron pair such as AlCl₃ and the like.

54 **[0011]** Any numerical values recited herein include all values from the lower value to the
55 upper value in increments of one unit provided that there is a separation of at least 2 units
56 between any lower value and any higher value. As an example, if it is stated that the amount of a
57 component or a value of a process variable such as, for example, temperature, pressure, time and
58 the like is, for example, from 1 to 90, preferably from 20 to 80, more preferably from 30 to 70, it
59 is intended that values such as 15 to 85, 22 to 68, 43 to 51, 30 to 32 and the like, are expressly
60 enumerated in this specification. For values which are less than one, one unit is considered to be
61 0.0001, 0.001, 0.01 or 0.1 as appropriate. These are only examples of what is specifically
62 intended and all possible combinations of numerical values between the lowest value and the
63 highest value enumerated are to be considered to be expressly stated in this application in a
64 similar manner.

65 **[0012]** The ionic liquids of the present invention may comprise one or more compounds.
66 Thus, the ionic liquid may be a pure compound or may be a mixture of compounds. Each
67 compound comprises an anion or a mixture of anions and a cation or a mixture of cations as
68 described below.

69 Anions

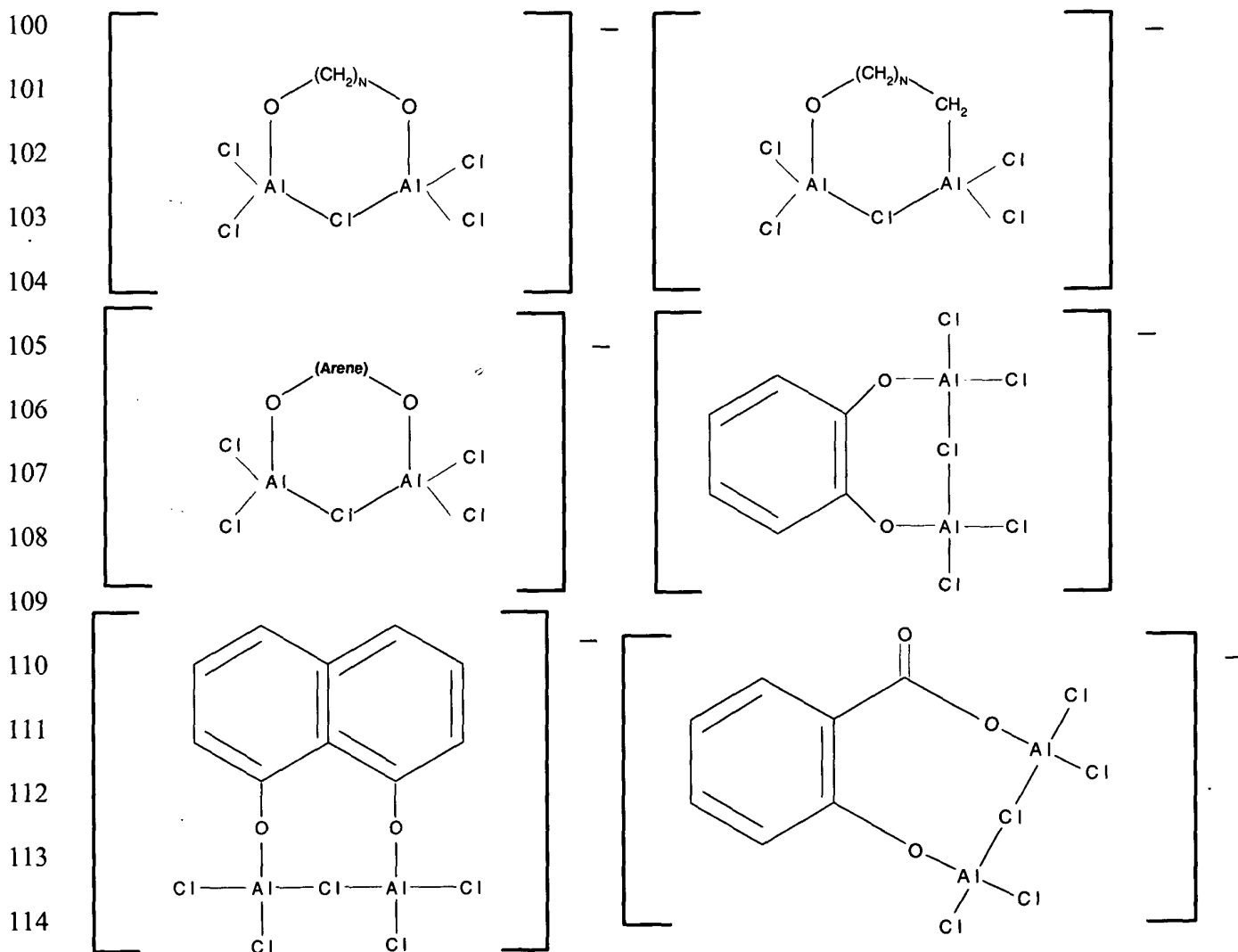
70 **[0013]** The anions of the present inventions typically have the formula Al_yR_{3y+1} wherein y is
71 greater than 0 and R is independently selected from an alkyl group or a halogen group. Y may
72 be an integer but it also includes decimals when there are non-stoichiometric amounts of the
73 aluminum anion. In these cases, the aluminum anion will be mixed with other anions such as
74 halides. Thus, ionic liquids of the present inventions include compositions comprising, for
75 example, a quaternary ammonium chloride mixed with a quaternary ammonium aluminum
76 chloride. The aluminum chloride can be, for example, tetrachloroaluminate or
77 heptachlorodialuminate.

78 **[0014]** The R group and the value of y in the anion are usually selected based on the desired
79 properties of the ionic liquid. For example, if the ionic liquid is going to be used as a Friedel-
80 Crafts catalyst then particularly preferred anions are aluminum chloride anions such as $AlCl_4$ and
81 Al_2Cl_7 .

82 **[0015]** When one or more R groups are a halogen group the halogen is preferably chloride,
83 bromide or iodide. When one or more R groups is an alkyl group then the alkyl group should
84 have a sufficient number of carbon atoms so that the ionic liquid has the desired properties. For
85 example, if the ionic liquid is to be used as a catalyst then the total number of carbon atoms in
86 the ionic liquid should be selected so as to maximize the catalyst's effectiveness and efficiency.
87 The total number of carbon atoms may also affect other properties of the ionic liquid such as
88 vapor pressure, dipole moment, polarity, etc.

89 **[0016]** In one embodiment, a carbon containing bridge between neighboring aluminum
90 atoms is used to stabilize a dialuminum anion contained in the ionic liquid. The carbon
91 containing bridge may contain alkyl, alcoxide and/or arene groups and substantially inhibit

92 leaching of aluminum trichloride into the surrounding composition. For example, the ionic
 93 liquid may be used as a reaction solvent and/or catalyst and it would typically be undesirable for
 94 aluminum trichloride to leach into the process stream. The organic bridge is preferably selected
 95 to sufficiently stabilize the dialuminate anion while maintaining sufficient activity for any desired
 96 catalytic functionality. The organic bridge is used to bond neighboring aluminum atoms that
 97 would otherwise be susceptible to leaching of aluminum trichloride. It is believed that the
 98 following anion structures would be useful to form ionic liquids while tending to prevent
 99 undesirable leaching of aluminum trichloride:



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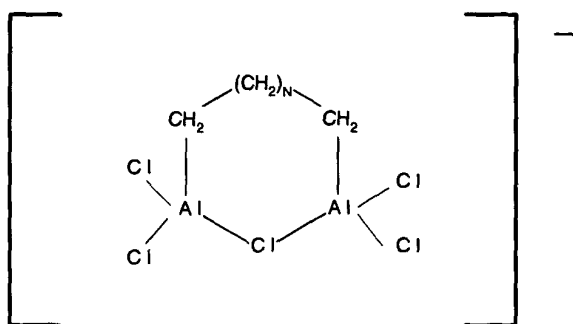
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Cations

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[0017] The cations of the compositions of the present inventions are generally selected from ammonium, sulfonium, and phosphonium cations wherein said cation has less than 14 total carbon atoms. By limiting the number of carbon atoms in the cation to less than 14 carbon atoms, an ionic liquid can be obtained which has a higher percentage of Al_yR_{3y+1} per unit volume. This often facilitates reactivity and typically makes the ionic liquid a much better catalyst. In addition, it is often preferred that the ammonium, sulfonium, and phosphonium cations be saturated to be most effective, convenient, or cost-effective as catalysts.

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[0018] A preferred cation is tetraalkylammonium. Depending on the desired ionic liquid properties it may be advantageous for one or more of the alkyl groups to be optionally substituted with one or more suitable substituents. Suitable substituents include, for example, halogens such as chloride, bromide, or iodide. Particularly preferred tetraalkylammonium cations include trimethylethyl ammonium, trimethyl chloromethyl ammonium, trimethylbutyl ammonium, and tributyl methyl ammonium. It is preferred that when the cation is triethylmethyl ammonium then the anion should be selected from aluminum bromide, or aluminum iodide.

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[0019] Another preferred cation is N-alkyl substituted saturated heterocycles such as piperidinium and morpholinium. Pyrrolidine-based cations can also be employed. In particular,

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138 piperidinium and pyrrolidine-based cations substituted on the nitrogen with an alkyl group (or
139 alkyl groups containing one or more ether groups or halide groups) such as $-(\text{CH}_2)_2\text{OMe}$, butyl,
140 or propyl are particularly beneficial. The cation may include ether functionality (e.g.,
141 $\text{NCH}_2\text{CH}_2\text{OCH}_3^+$). The cation may include halogenated alkyl groups.

142 [0020] It has been found that several factors can be used to predict the ability of a given
143 cation to form a salt that is liquid at or near ambient temperature. Cations having between 5 and
144 11 total carbon atoms, in the absence of heterocyclic structures, have been found to be useful in
145 making molten salts with desirable melting point and phase behavior properties. Further, cations
146 that are non-tetrahedrally symmetric tend to more readily form near ambient temperature molten
147 salts. Additionally, the anion and the cation are preferably present in a molar ratio of about 2:1,
148 respectively, \pm about 10% (i.e., about 1.8 to 2.2 moles of anion for every mole of cation).

149 Processes to make Compositions of the Present Inventions

150 [0021] The ionic liquids of the present inventions may be conveniently made by a number of
151 different processes. One process which is suitable for making ionic liquids or mixtures of the
152 present inventions comprises reacting a halide of the desired cation with a Lewis acid in the
153 presence of an optional solvent. That is, the process for preparing a Lewis acid ionic liquid
154 composition of the present inventions often comprises mixing an ammonium, sulfonium, or
155 phosphonium halide with $\text{Al}_y\text{R}_{3y+1}$. The ammonium, sulfonium, or phosphonium halide
156 preferably comprises less than 14 total carbon atoms.

157 [0022] The manner of contacting the two or more compounds to form the ionic liquid is not
158 particularly important so long as the desired reaction occurs. Generally, the compounds can be
159 mixed in any order, can be formed *in situ*, or can be mixed together with a solvent which is at
160 least partially miscible and does not significantly react with any of the compounds. Preferred

161 solvents include substances that give good reflux conditions like cyclohexane, alkanes, toluene,
162 or mixtures thereof.

163 **[0023]** The starting compounds are often readily available and, in addition, many syntheses
164 are available to those skilled in the art to make the desired starting compounds. The mixing
165 conditions may vary depending on the specific compounds employed and the desired product. In
166 most instances, it is acceptable to contact the compounds and the optional solvent at ambient
167 pressure and a temperature high enough for the reaction to occur efficiently but not so high as to
168 decompose or boil off any starting compound.

169 **[0024]** The manner in which the desired temperature is achieved and maintained is not
170 particularly critical. Often any heating element may be employed as the compounds are mixed
171 or the starting compounds can be heated separately and then mixed. Similarly, any vessel or
172 reactor can be employed so long as it is of adequate size and material. Often it is beneficial to
173 employ a stirring means to facilitate the reaction.

174 **[0025]** Generally, the temperature is maintained for at least a sufficient time until the desired
175 reaction has occurred to the desired extent. In some instances, it may be desirable to maintain
176 the temperature for a longer time than it takes to complete the reaction. In this manner, any
177 lower boiling components that are formed as byproducts or present as solvents can be removed
178 by boiling if the temperature is high enough to do so.

179 **[0026]** The amount of each of the starting compounds may vary depending upon the desired
180 yield. In general, since the reaction is very exothermic the ratio of ammonium, sulfonium, or
181 phosphonium halide to Al_yR_{3y+1} should be selected so that any heat produced by the reaction is
182 controlled. While for some starting compounds this may be a stoichiometric ratio, generally, one
183 of the starting compounds should be in molar excess to most effectively control the heat of the

184 reaction. However, as one skilled in the art will appreciate, different reaction conditions may
185 alter the ratio of reactants at which the optimum yield and optimum control of reaction heat
186 occurs. In addition, if an ionic liquid is desired with a higher percentage of Al_yR_{3y+1} then a molar
187 amounts of the aluminum starting material should be increased.

188 [0027] If one desires to make an ionic liquid mixture comprising two or more different salts,
189 then it is readily accomplished by employing a mixture of three or more different compounds so
190 that a variety of salts are formed. The resulting ionic liquid salt mixture can then be used as a
191 mixture or, if desired, individual salts can be separated by routine means.

192 [0028] If necessary, the ionic liquid or ionic liquid mixture may be recovered from the
193 solvent and/or reaction mixture by any suitable means the most efficient of which may vary
194 depending upon the type and desired purity of the ionic liquid or mixture. Preferable means of
195 recovery include rotary evaporation or distillation, azeotropic distillation, ion chromatography,
196 liquid liquid extraction, crystallization, pervaporization, drying agents, and reverse osmosis.

197 [0029] In one embodiment, azeotropic distillation can be employed to remove water from the
198 source of cation prior to the addition of a chloroaluminate to form the ionic liquid. For example,
199 amine, phosphine, or mercaptan can be reacted with an alkyl halide in an organic solvent to form
200 a cation as a halide salt. The organic solvent is preferably a hydrocarbon. Exemplary organic
201 solvents include cyclohexane, toluene, octane, and hexane. Heat can then be added to the
202 mixture to cause the organic solvent to boil, thereby forming an azeotrope between the organic
203 solvent and any water present. Most or all of the water is preferably removed by azeotropic
204 distillation. The halide salt (source of cation) can then be reacted with the chloroaluminate
205 (source of anion) to form an ionic liquid. The solvent is preferably refluxed to remove at least a
206 portion of heat generated by reaction via the boiling and condensation of the solvent.

207 **[0030]** The organic solvent can be removed from the ionic liquid by use of a liquid
208 extraction. The organic solvent preferably forms a barrier layer on top of the ionic liquid prior to
209 separation to inhibit moisture from the air from contacting the ionic liquid. After the liquid
210 extraction, the residual organic solvent may be separated from the ionic liquid via distillation
211 under vacuum conditions. The organic solvent, which may contain impurities from the reactants
212 (such as aluminum chloride), is preferably washed with water prior to being recycled back into
213 the reaction mixture for reuse.

214 Characteristics and Uses of Ionic Liquids of the Present Inventions

215 **[0031]** The purity of ionic liquids produced by the processes of this inventions can often be
216 greater than 50%, preferably greater than 60%, more preferably greater than 70%, most
217 preferably greater than 80%. This is often advantageous for processes that require high purity
218 materials such as in the electronics industry. The ionic liquids are useful in many processes as a
219 substitute for an organic solvent or catalyst or in mixtures with one or more added solvents or
220 catalysts. Some ionic liquids of the present inventions are particularly useful catalysts for
221 dimerization or trimerization of olefins, for Friedel-Crafts reactions, or for hydrocarbon cracking.
222 Further, the ionic liquids of the present invention are often highly reactive and even react with
223 water.

224 **[0032]** The following examples are not intended to limit the inventions, but rather, are
225 intended only to illustrate a few specific ways the instant inventions may be employed.

226 **[0033] Example 1- Synthesis of Trimethylethyl Ammonium Aluminum Chloride**

227 **[0034]** Trimethylethylammonium chloride (940 g) was added to 1 liter cyclohexane in a 3
228 neck flask fitted with a thermocouple, a solid addition funnel, and a Dean-Stark trap with a reflux
229 condenser. The mixture was heated until the solvent boiled and the reflux is continued until no

230 more water collected in the trap. At this point, the trap and the heating mantle were removed
 231 and AlCl₃ was added (2009 g) gradually over several hours. The mixture gradually reacted to
 232 form a lower liquid layer with unreacted solid tetraalkylammonium chloride, which disappeared
 233 as the AlCl₃ was added. By the time the AlCl₃ addition was complete, all the solids had
 234 dissolved, and the mixture comprised two liquid phases. The mixture was allowed to cool, and
 235 the contents of the flask were transferred to a separatory funnel. The lower layer was collected
 236 under nitrogen, and the cyclohexane that was still dissolved in the ionic liquid was stripped off
 237 under vacuum. The yield of the final product (trimethylethylammonium
 238 heptachlorodialuminate) was nearly quantitative.

239 **[0035] Examples 2-5**

240 The ionic liquids of Examples 2-5 in Table 1 below were made substantially as in the
 241 same manner as Example 1 except that the starting compounds of Table 1 are employed.

242 **[0036] Table 1**

Example	Starting compound	Ionic Liquid
2	N-alkyl substituted piperidinium chloride	N-alkyl substituted piperidinium heptachlorodialuminate
3	trimethyl chloromethyl ammonium chloride	trimethyl chloromethyl ammonium heptachlorodialuminate
4	trimethylbutyl ammonium chloride	trimethylbutyl ammonium heptachlorodialuminate
5	tributyl methyl ammonium chloride	tributyl methyl ammonium heptachlorodialuminate

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244 Of course in any of the aforementioned examples the molar ratio of starting compounds can be
245 adjusted to vary the ratio of specific cations and specific anions in the product. In addition, the
246 molar ratios and starting materials can be varied so that the anion of the ionic liquid is, for
247 example, tetrachloroaluminate, tetrabromoaluminate or the like.

248 **[0037] Examples 6-12**

249 The ionic liquids of Examples 6-12 in Table 2 below were made substantially as in the
250 same manner as Example 1 except that the ammonium salts of Table 2 were employed with
251 AlCl₃ in the amounts detailed below. In some cases, vacuum drying was used instead of
252 azeotropic distillation to dry the chloride salt.

253 **[0038] Table 2**

Example	Ammonium Salt	Moles of Ammonium Salt	Moles of AlCl ₃	Product
6	MeBu ₃ N Cl	0.090	0.193	liquid
7	Me ₃ PentylN Cl	0.006	0.013	liquid
8	Me ₃ ButylN Cl	0.008	0.016	liquid
9	MeEt ₃ N Cl	0.006	0.012	liquid
10	Me ₂ Et ₂ N Cl	0.078	0.157	liquid
11	Cl-CH ₂ -NMe ₃ Cl	0.025	0.049	liquid
12	N-methyl-N-Butyl Pyrolidinium Cl	0.042	0.084	liquid

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